AIR QUALITY PRYDEN

Annual Report, 1979

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AIR QUALITY

DRYDEN

Annual Report, 1979

TECHNICAL SUPPORT SECTION
NORTHWESTERN REGION
ONTARIO MINISTRY OF THE ENVIRONMENT
September, 1980



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SUMMARY

The Ministry's air quality assessment programme in Dryden continued in 1979 with investigations similar to those conducted since 1970.

Residual mercury in vegetation, in experimentally exposed moss, and in soil near a local kraft pulp mill and adjacent chlor-alkali plant persisted at concentrations slightly above normal. However, for the first time since the chlor-alkali plant was converted in late 1975 to a non-mercury process, mercury levels in snow in the surrounding area were all below the analytical detection limit. All available evidence now shows that mercury has declined to near normal concentrations in the atmospheric and terrestrial environment around the Dryden mill.

In mid-July, abnormal emissions of chlorine or chlorine dioxide from the mill resulted in damage to vegetation in a 12-hectare area southeast of the mill. Typical chlorine injury symptoms were observed on vegetation in at least 12 residential gardens, and two complaints were registered.

Fallout of particulate matter (dustfall) continued to decline, and there was substantial compliance with Ontario air quality objectives for dustfall in the town area. Calcium, chloride, sodium and sulphate in snow or in moss were moderately elevated on or adjacent to mill property, but acceptable in the surrounding area. Dustfall in Dryden has decreased about 50 percent in the past 4 years, largely because of emission controls installed at the mill.

Offensive odours, caused by emissions of total reduced sulphur (TRS) from the kraft mill, were frequently recorded at high concentrations in the town centre. The Ontario guideline for TRS was exceeded during 391 hours, or just over 8 percent of the time. The maximum reading was nearly nine times the guideline. A control order recently served on the mill should result in substantial reductions in community odour levels by 1984.

INTRODUCTION

Air quality studies in Dryden were first undertaken by the Ministry of the Environment in 1970 to assess the effects of atmospheric emissions from a bleached kraft pulp mill and associated mercury-cell chlor-alkali plant. Reports of these investigations (1, 2, 3, 4) showed that levels of mercury, particulate fallout, and offensive odours in the vicinity of the mill were often significantly above normal.

The Ministry's 1979 assessment programme, described in this report, included vegetation and soil studies, a moss exposure experiment, snow sampling, and air quality monitoring.

VEGETATION AND SOIL ASSESSMENT

VEGETATION

Triplicate samples of trembling aspen (<u>Populus tremuloides</u>) and Manitoba maple (<u>Acer negundo</u>) foliage were collected in July from 18 sites in Dryden (Figure 1) and from two control locations several kilometres from the town area. The purpose of the survey was to document current levels of mercury in local vegetation following conversion of the chlor-alkali plant to a non-mercury process in late 1975. Sampling and sample processing procedures were outlined in an earlier report (3). Analysis for mercury was conducted at the Ministry's Thunder Bay laboratory.

Foliar mercury concentrations, listed in Table 1, were little different from those for other years since 1975 (Table 2). The highest levels, mostly near the mill, were only marginally above normal background. Since the situation now appears stable, no further routine vegetation sampling for mercury is scheduled.

In mid-July, an accidental release of chlorine or chlorine dioxide from the mill's bleachery resulted in injury to trees. shrubs and garden vegetation in an area of about 11.5 ha (hectares) southeast of the mill. Two complaints of air pollution damage to vegetation were received from local A very small area (0.5 ha) of chlorine-like injury symptoms on red osier (Cornus stolonifera) shrubs was also discovered a week later on company property near the chemical Whether this injury was from the same or a different fumigation is unknown. Analysis of tree foliage, carried out by the Ministry's central laboratory, showed moderately elevated chloride concentrations in samples in the study area, but there was no obvious gradient with changes in distance from the mill, nor were there any significant differences from results in 1972 and 1975 (1). Other than the chlorine injury which occurred in July, there was no other evidence of air pollution effects on vegetation, nor any sign of damage from a forest tent caterpillar infestation similar to that recorded in 1978.

SOIL

Surface soil, to a depth of 5 cm (centimetres), was collected by standard Ministry sampling procedures from the same sites where vegetation had been obtained. The mercury content of soil (Table 1) was rarely above the level considered normal for Ontario soils. Two exceptions were recorded: an elevated reading near the chemical plant (where abnormal mercury was expected), and an unexpected excessive value at site 12, west of the mill. The cause of the high concentration at this location is unknown, and a further small-scale survey is planned to investigate. Other than the exceptions noted, mercury levels at other sampling points were normal, and there were no major differences from other years (Table 2).

MOSS EXPOSURE

Moss has been found effective in trapping and retaining some types of air pollutants. At the sites shown in Figure 1, small quantities of Sphagnum moss were exposed for 41 days from June 13 to July 24. The field and laboratory procedures are described in the 1976 report (2). Calcium, mercury and sodium in moss were analysed at the Thunder Bay laboratory and chloride was determined at the Ministry's Toronto laboratory. The data are presented in Table 3. Mercury concentrations in moss were much the same in 1979 as they were in 1978, although it should be noted that the exposure periods were different. These data confirm the findings from vegetation samples which showed that there was very little airborne mercury around the mill. Calcium was slightly elevated near the mill, but near background levels Chloride and sodium concentrations significantly elevated but, even in these cases, the higher readings were mostly restricted to company property. Figure 3 shows the distribution pattern for chloride, which was similar to that for sodium.

SNOW SAMPLING

Snow sampling is used to identify and determine the extent of particulate fallout around some industrial sources. Past surveys at Dryden have shown that calcium, mercury, sodium and sulphate have been well above normal concentrations expected in uncontaminated snow.

In February, 1979, duplicate core samples were obtained from snow at 18 sites (Figure 4), and from two control locations outside Dryden. Normal Ministry sampling and sample processing procedures were followed (2). All analyses were performed at the Thunder Bay laboratory.

The most noteworthy result from the 1979 survey was the uniform occurrence of mercury at levels below the detection limit (Table 4). This was the first occasion, since the chlor-alkali plant conversion in late 1975, that this satisfactory state had been reached. Figures 5a and 5b clearly illustrate the difference between the situation in 1975 and 1979. A few elevated readings were found for calcium, sodium, and sulphate, but all the high values were on or very close to mill property, and well below levels up to 1977. High pH values corresponded to high calcium concentrations. There was no visible particulate matter in snow except at sites 6, 10, 11 and 27, where the highest calcium, sodium and sulphate levels occurred. At these locations, there was some brown particulate matter in horizontal bands below the snow surface. Since the latest data indicate very little contamination in snow at Dryden, no further snow sampling is planned for the near future.

AIR QUALITY MONITORING

DUSTFALL

Dustfall is particulate matter that settles out from the atmosphere by gravity. The measurement method is described in an earlier report (3). Total dustfall and soluble sulphate in dustfall were determined at the Ministry's Thunder Bay laboratory for the seven sites (Figure 6) where measurements were made in 1979.

Table 4 shows dustfall results for the year. Only 10 percent of all monthly values were above the air quality objective, and no reading was considered excessive. The highest levels in April, May and July at station 61026 were attributed mainly to road dust from an adjacent unpaved lane and car park. Four of the seven sites met the annual objective, and three were marginally above. Sulphate concentrations were all within the range considered normal. Trace amounts of bark char were occasionally noted in dustfall jars at the five sites south of Highway 17.

Table 6 illustrates the trend of declining dustfall and sulphate in dustfall from 1976 to 1979. This improvement is attributed principally to the environmental controls installed at the mill in early 1977. In the period covered by Table 6, total dustfall decreased 50 percent and sulphate 80 percent. Since all significant sources of particulate emissions at the mill are now controlled, no further improvement in average community dustfall levels are anticipated.

SULPHATION RATE

Monthly sulphation measurements, based on the method described in the 1978 report (4), provide an estimate of average levels of sulphur-containing gases in the atmosphere. In Dryden, the sulphation plates respond mainly to reduced sulphur compounds, since previous surveys have established (1) that sulphur dioxide concentrations in this area are negligible.

Results for the four sulphation monitoring stations maintained in 1979 (Table 7) showed little change from 1978. Based on past experience, a reading of 0.20 mg $\rm SO_3/100~cm^2/day$ (milligrams of $\rm SO_3$ per hundred square centimetres per day) indicates that unacceptably high odour levels are present. Readings above this level were recorded from time to time, with highest values near the mill. An extremely high sulphation rate was obtained in July at station 61023, approximately 300 metres east of the mill.

TOTAL REDUCED SULPHUR

Total reduced sulphur (TRS) comprises a group of sulphur-containing gases commonly associated with emissions from kraft pulp mills. At very low concentrations, any of these gases will create offensive odours. At higher levels, TRS may darken paint, damage vegetation, or cause temporary discomfort to individuals sensitive to this group of pollutants.

The Ministry measures TRS continuously in Dryden with an instrument located at 56 King Street (station 61026). monitor responds to most of the main components of TRS: hydrogen sulphide, methyl and ethyl mercaptan and dimethyl sulphide. Data for 1979 are summarized in Table 8 and plotted in Figure 7. records were obtained for January, February and October because of equipment malfunction. During the 9 months of valid data, there were 391 hours (8.2% of the total) during which the Ontario guideline of 27 ppb (parts per billion) was exceeded. Comparable figures for 1978 and 1977 were 400 hours (5.9%) and 270 hours The proportion of undesirably high TRS values has (3.7%).therefore increased during the past three years. The maximum hourly average in 1979 was 236 ppb, or nearly nine times the No data on wind directions were available for 1979, quideline. but information for other years (3, 4) showed that virtually all the measurable TRS at the King Street monitoring station could be traced to emissions from the kraft mill.

At the highest levels recorded in Dryden, TRS might cause temporary discomfort to local residents. This effect would be mitigated by reduced emissions from the mill or by a change in wind direction. The Ministry is not aware of any evidence linking chronic health effects to elevated TRS concentrations in communities near kraft pulp mills. A recently issued control order stipulates that the discharge of all odour causing contaminants from the Dryden mill must comply with Ontario regulations by 1984.

ACKNOWLEDGEMENT

The Ministry wishes to thank staff of the Dingwall Medical Group, Dryden, for assistance in operating the TRS monitor.

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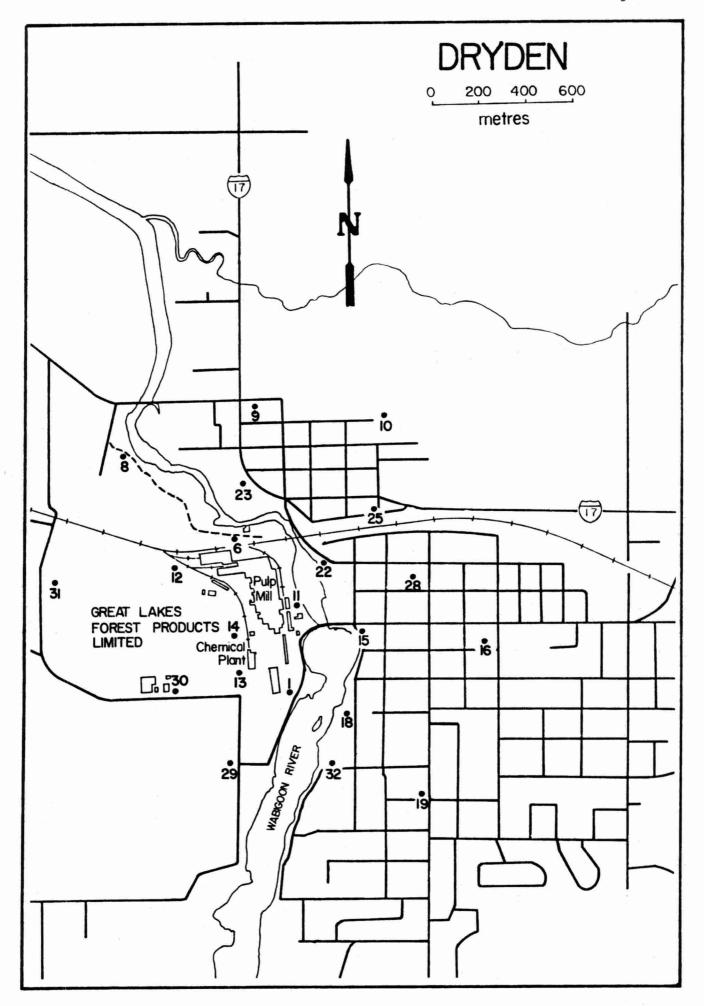


Figure 1. Vegetation, soil sampling, and moss exposure sites, 1979.

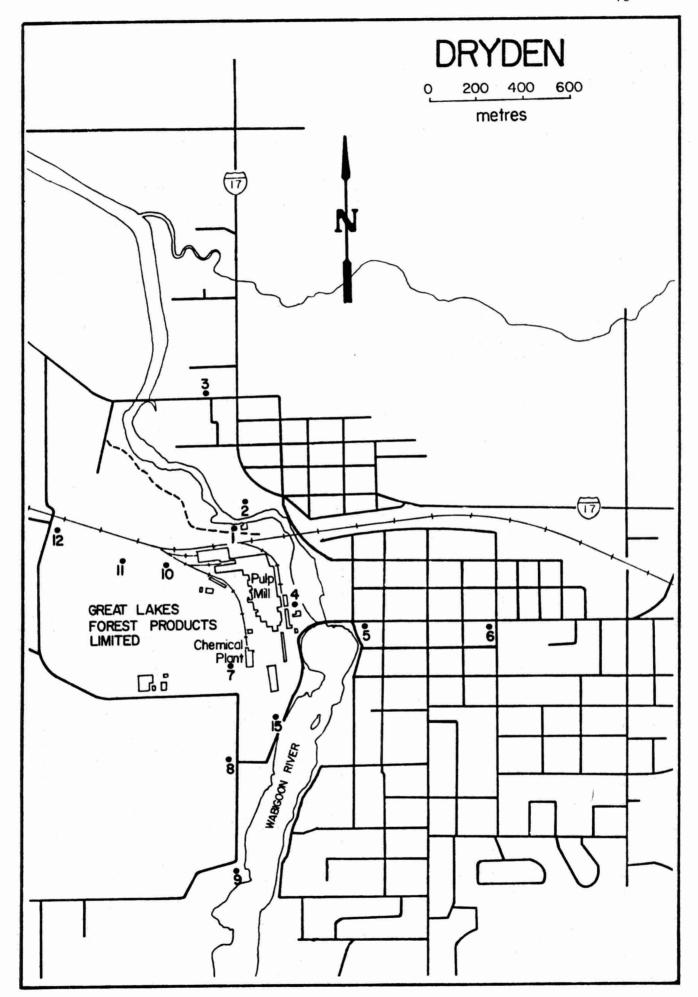


Figure 2. Vegetation and soil sampling sites for inter-year comparison (Table 2).

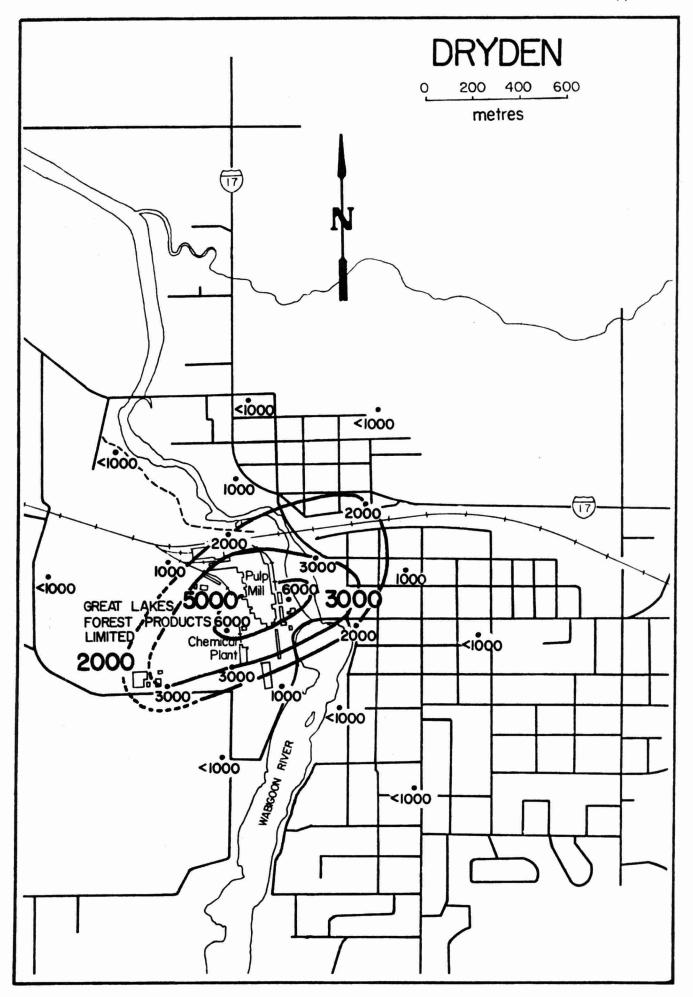


Figure 3. Levels of chloride ($\mu g/g$, dry weight) in moss exposed from June I3 to July 24 , I979.

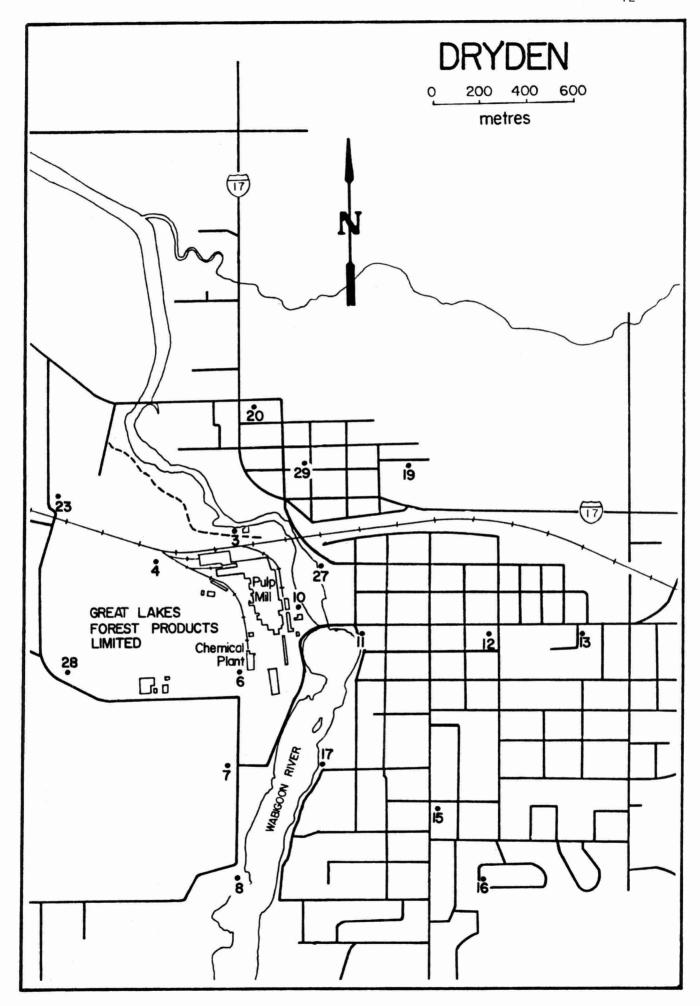


Figure 4. Snow sampling sites, February, 1979.



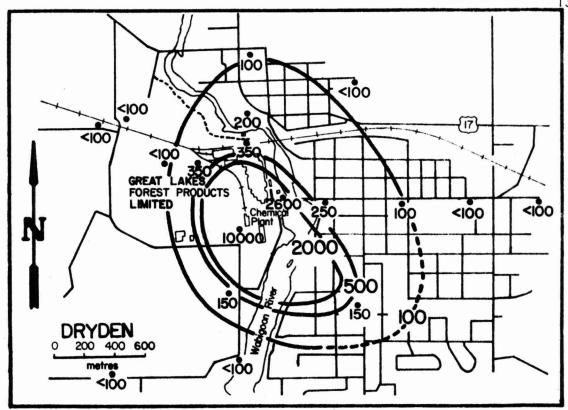


Figure 5a. Average concentrations of mercury (ng/1) in snow, 1975.

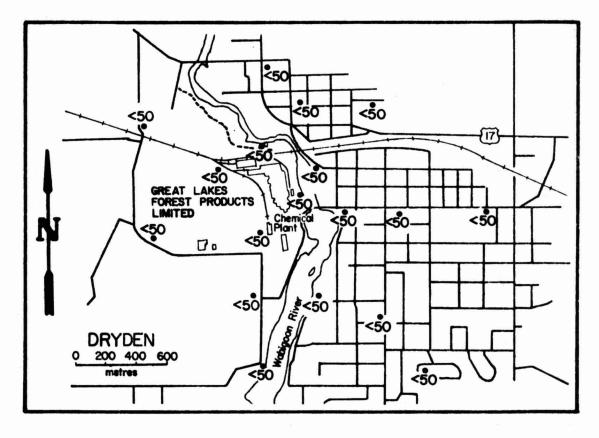


Figure 5b. Average concentrations of mercury (ng/1) in snow, 1979.

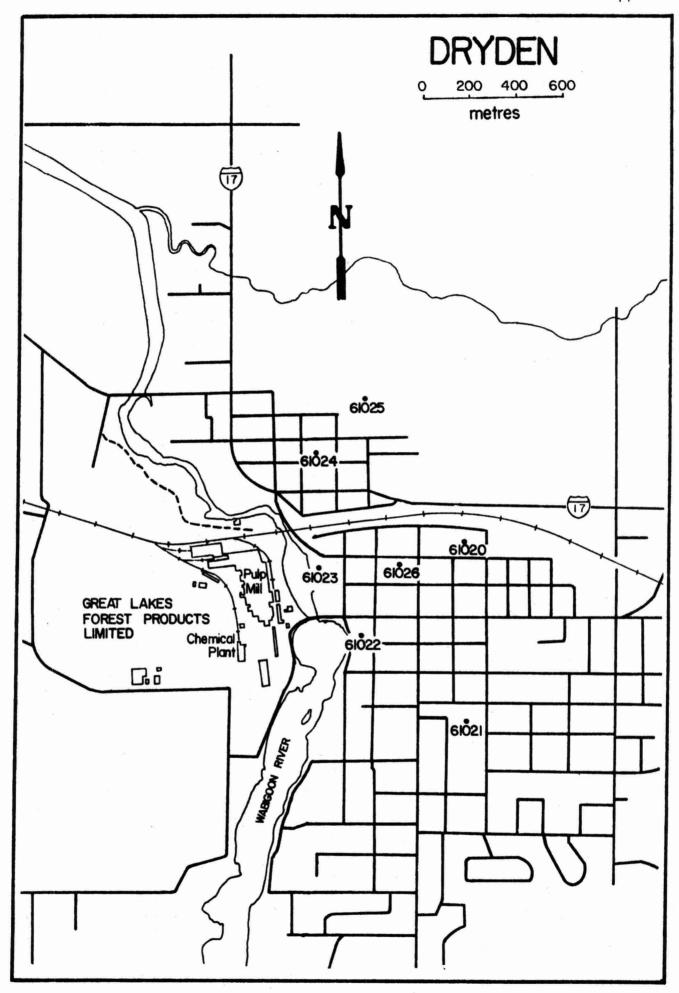


Figure 6. Air quality monitoring sites, 1979.

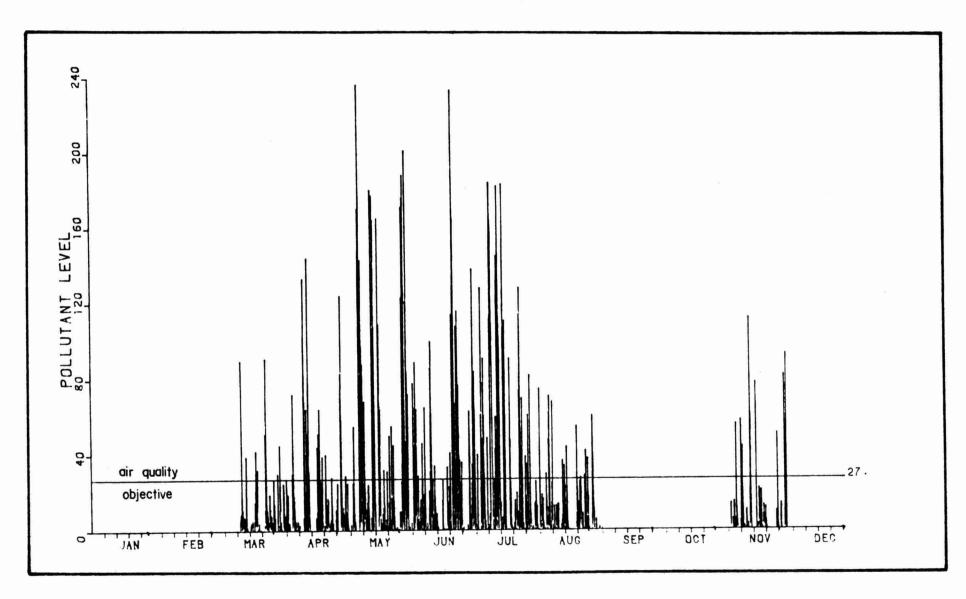


Figure 7. Hourly average TRS concentrations (ppb), station 61026, Dryden, 1979.

TABLE 1. Chloride and mercury concentrations (dry weight basis) in tree foliage and soil collected in Dryden, July, 1979.

		Foliage							
Sampling sit (Figure 1)	e Chloride	(%) Mercury (ı	ng/g) Mercury (ng/g						
1	0.24	100	190						
6	0.30	150	60						
8	0.29	120	90						
9	0.33	80	60						
10			20						
11	0.26	130	70						
12	0.20	50	19000						
13	0.21	150	4700						
15	0.20	80	90						
16	0.13	70	40						
18	0.12	70	60						
19	0.08	60	50						
22	0.18	70	130						
23	0.16	35	60						
25	0.30	100	190						
28	0.19	70							
29	0.28	30	70						
31	0.14	70	90						
32	0.29	80	60						
controls	0.09	30	30						
normal background		< 100	< 300						

TABLE 2. Average mercury levels (ng/g, dry weight basis) in tree foliage and surface soil (0-5 cm) in Dryden, 1975 to 1979.

Site		Ve	getatio	n				Soil		
(Figure 2)	1975	1976	1977	1978	1979	1975	1976	1977	1978	1979
1	1840	100	80	60	150	140	50	340	360	60
2	1400	110	80	60	40	40	70	50	30	60
3	510	180	90	40	80	30	30	40	70	60
4				160	130	250	390	470	180	70
5			80	90	80	110	130	90	120	90
6			50	50	70	140	50	50	60	40
7	460	650	210	110	150	1200	1900	1300	2300	4700
8	50	50	40	20	30	50	30	30	20	70
9	60	60	50			50	40	40		
10	510	160	60	80	50	200	340	270	130	19000
11	380	90	60			180	300	120		
12	140	30	40	30	70	70	100	110	60	90
15		120	60	60	100		370	50	40	190
controls	20	30	20	20	30	50	20	40	40	30
normal background	< 100	< 100	< 100	< 100	< 100	< 300	< 300	< 300	< 300	< 300

TABLE 3. Concentrations, dry weight basis, of calcium, chloride, mercury and sodium in moss exposed from June 13 to July 24, 1979.

Site (Figure 1)	Calcium (%)	Chloride (%)	Mercury (ng/g)	S odiu m (μg/g)
1	1.4	0.1	100	510
6	1.3	0.2	90	330
8	2.0	<0.1	80	310
9	1.2	<0.1	60	250
10	1.2	<0.1	80	330
11	2.3	0.6	190	5500
12	1.5	0.1	120	810
13	1.3	0.3	180	840
14	1.4	0.6	210	1900
15	1.3	0.2	130	700
16	1.3	<0.1	120	150
18	1.4	< 0.1	120	240
19	1.6	< 0.1	130	150
22	1.9	0.3	170	4400
23	1.2	0.1	140	560
25	1.3	0.2	130	630
28	1.4	0.1	120	440
29	1.4	<0.1	110	390
30	1.5	0.3	120	980
31	1.2	< 0.1	120	200
exposed controls	1.2	<0.1	120	120
unexposed controls	1.2	<0.1	110	200

TABLE 4. Average levels of calcium, mercury, sodium, sulphate and pH in meltwater from snow samples collected in Dryden in February, 1979.

Site	Calcium (mg/l)	Mercury (ng/1)	Sodium (mg/1)	Sulphate (mg/l)	рН
3	7	< 50	3	5	8.9
4	10	< 50	3	3	9.6
6	10	< 50	3	5	8.1
7	6	< 50	2	3	7.9
8	3	< 50	1	2	7.2
10	52	< 50	17	14	11.1
11	7	< 50	7	6	9.6
12	7	< 50	2	2	9.0
13	4	< 50	2	1	7.7
15	4	< 50	2	2	7.4
16	3	< 50	1	1	7.4
17	4	< 50	2	2	8.3
19	8	< 50	2	2	9.0
20	4	< 50	4	2	7.0
23	3	< 50	1	3	7.6
27	12	< 50	8	10	10.5
28	4	< 50	2	2	8.0
29	6	< 50	2	2	8.5
controls	, 1	<50	< 1	< 1	4.7
normal background	< 5	< 500	< 5	< 5	

TABLE 5. Total dustfall $(g/m^2/30 \text{ days})$, Dryden, 1979.

Station	Location	Distance (metres) and direction from source	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	0ct	Nov	Dec	Mean
61020 61021 61022 61023 61024 61025 61026	Kirkpatrick/Queen Casimir/St. Charles Earl/Albert King/Wabigoon River Mary/Florence Park/Second 56 King Street	895 ENE 1010 ESE 430 ESE 305 NE 735 NNE 960 NNE 625 ENE	- 1.5 0.8	2.2 0.9 0.6 0.6 0.6	2.4 3.9 - 2.7 0.8 2.3	5.4 4.0 5.1 5.2 4.3 7.7 7.8	6.8 3.9 4.0 3.9 3.8 4.3 9.2	4.5 5.7 3.7 6.8 7.0 2.4 5.6	6.0 6.9 4.3 6.4 3.3 2.1 8.0	4.9 3.4 3.5 10.3 2.7 2.4 6.4	5.6 3.2 2.6 4.8 3.5 4.7 7.4	4.3 8.7 4.0 5.0 3.0 2.9 6.8	1.7 2.9 3.0 7.7 - 2.3 3.4	0.7 - 1.2 - 0.4 0.2 1.4	3.9 4.7 3.2 5.3 2.8 2.7 5.4

 $^{^{}a}$ source arbitrarily designated as recovery furnace stack, Great Lakes Forest Products Limited kraft pulp mill b values exceeding maximum acceptable levels of 7.0 (monthly) or 4.6 (annual average) are underlined

TABLE 6. Comparison between average annual dustfall $(g/m^2/30 \text{ days})$ at Dryden, 1976 to 1979.

		All stations						
Year	61020	61021	61022	61023	61024	61025	Total dustfall	Sulphate
1976 1977	8.0 5.8	6.3	9.8	11.5	5.9	4.5	7.7 6.4	1.6
1978 1979	4.7 3.9	5.1 4.7	6.0	4.6 5.3	2.9	2.5	4.3	0.2

TABLE 7. Sulphation rate (mg $SO_3/100 \text{ cm}^2/\text{day}$), Dryden, 1979.

Station	Location	Distance (metres) and direction from source	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	0ct	Nov	Dec	Mean
61021 61023 61025 61026	Casimir/St. Charles King/Wabigoon Park/Second 56 King Street	1010 ESE 305 NE 960 NNE 625 ENE	.10 .27 .08 .15	.02 .11 .05 .12	.07 .22 .07	.11 .23 .04 .07	.15 .71 .12 .27	.14 .52 .26	.11 1.35 .33 .72	.16 .46 .13 .18	.30 .60 .25 .36	.16 .14 .07 .28	.16 .30 .13	.15 .30 .10 .15	.14 .44 .14 .23

^asource arbitrarily designated as recovery furnace stack, Great Lakes Forest Products Limited kraft pulp mill

TABLE 8. Distribution of total reduced sulphur readings (ppb, hourly averages) in 1979 at station 61026, Dryden.

	Days	Numb	er of r	eadings	for conce	ntrations	of:	Maximum	value:			
Month	of data	0-10	11-27	28-50	51-100	101-300	>300	Hour	Day			
Jan	e				no data							
Feb		no data										
Mar	18	367	21	5	6	0	0	91	17			
Apr	30	608	63	24	10	3	0	144	28			
May	31	598	62	19	23	33	0	236	74			
Jun	30	541	84	48	28	18	0	233	51			
Ju 1	31	582	41	34	39	42	0	184	109			
Au g	31	636	78	16	12	0	0	82	20			
Sep	4	100	4	5	3	0	0	61	19			
0ct					no data							
Nov	22	484	38	5	9	1	0	112	22			
Dec	3	73	5	3	5	0	0	93	18			
YEAR	200	3989	396	159	135	97	0	236	109			

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